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The Influence of an Electric Field on the Viscosity of Aeolotropic Liquids

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The viscosity of aeolotropic liquids between two plates has been found to increase when an electric field, steady or alternating, is applied perpendicularly to the plates; this effect is probably due to real or apparent orientation of the axis of the swarms parallel to the electric field. A change of electrical conductivity under shearing stress has also been found. Ordinary isotropic insulating liquids show some apparent decrease in viscosity with a steady field, but this is probably due to electrolysis.

THE liquids called mesomorphic melts, liquid crystals or aeolotropic liquids display a number of anomalies in comparison with ordinary liquids. Of the most striking of these anomalies we mention the following.

Viscosity shows a peculiar variation with the temperature. The phenomenon was studied at an early stage in the history of the mesomorphic liquids and was used in order to disprove the emulsion theory.

The electrical conductivity due to the presence of dissolved electrolyte is changed by the action of a magnetic field, a phenomenon discovered by The. Svedberg.[1] The influence of a magnetic or an electric field on the light absorption has been studied by the author.[2] Even mechanical action changes the light absorption.[2] The influence of a magnetic field on the diffusion constant of a solute has been investigated by Svedberg.[3] These effects are only found in liquids of the nematic type. For several other phenomena I refer to the summary published by Oseen.[4]

It is therefore perhaps not astonishing that the viscosity of certain liquid crystals of the nematic type shows a marked dependence on an electric field. As regards ordinary liquids it has generally been assumed that such an action does not exist. This view is in accordance with theoretical con-

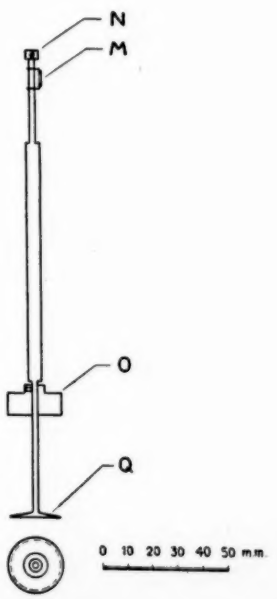

FIG. 1. Rotor. *N*, clamp; *M*, mirror; *Q*, disk; *O*, weight.

[1] The. Svedberg, *Über die Elektrizitätsleitung in anisotropen Flüssigkeiten*, Ann. d. Physik. **44**, 1121 (1914).
[2] Y. Björnståhl, *Untersuchungen über anisotrope Flüssigkeiten*, Ann. d. Physik **56**, 161 (1918).
[3] The. Svedberg, *Diffusion in anisotropen Flüssigkeiten*. Kolloid Zeits. **22**, 68 (1918).
[4] C. W. Oseen, *Die anisotropen Flüssigkeiten* (Fortschritte der Chemie, Physik und physikalischen Chemie, **20**, No. 2).

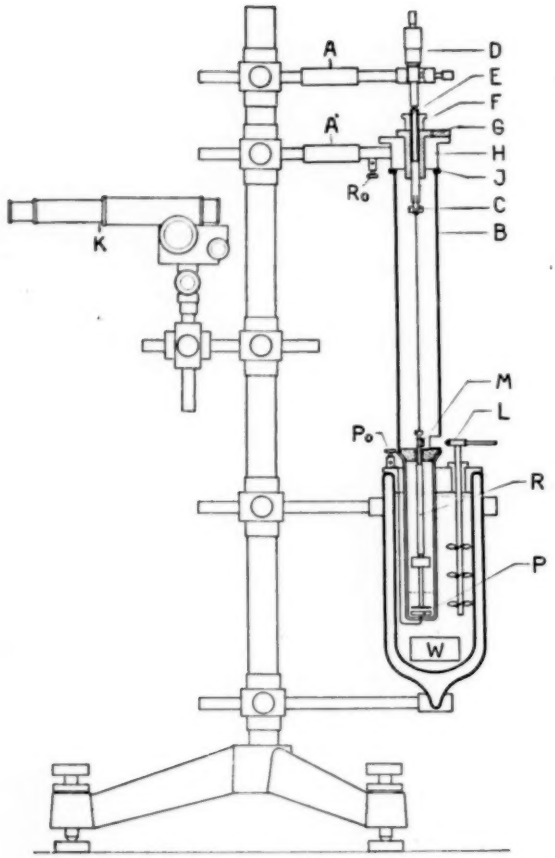

FIG. 2. Schematic diagram of the apparatus. *R*, rotor; *P*, electrode; *M*, mirror; *W*, heater; *L*, stirrer; *B*, case; *H*, torsion head; *G*, pointer; *C*, chuck; *D*, micrometer head; *A*, insulator; *K*, telescope; *J*, *J* insulators.

siderations.[5] I will show, however, that there are certain apparent exceptions to this rule.

EXPERIMENTAL ARRANGEMENT

The apparatus consisted in principle of a rotor, a disk suspended by a wire and immersed in the liquid to be investigated, and a fixed plate below the disk. The two plates formed the two terminals. The damped oscillations of the rotor were studied.

The rotor was made of brass (Fig. 1). A clamp *N* and a mirror *M* were fixed at the top. The weight *O* was added in order to increase the moment of inertia. The disk *Q* was gold-plated in some cases.

A sectional drawing of the whole arrangement is given in Fig. 2. The rotor *R* was suspended by a phosphor bronze wire, fixed in the chuck *C*, which was attached to the torsion head *H*. One part of this could be rotated and was provided with a pointer *G*. The screw *E* could be moved up and down by means of the nut *F*. The position of the pointer *G* could be read on a dial *H*. The torsion head was insulated from the rod of the support by means of the insulator *A* and from the case by means of *J*. The distance between the rotor disk and the plate *P* was determined with the aid of the micrometer head *D*, on which 0.01 mm could be read. The reading was checked by means of a telescope *K*, which was provided with a micrometric eyepiece.

The liquid was contained in a cylindrical vessel of Jena Normal Glass, at the bottom of which a brass plate *P* was fixed by means of a platinum bolt. This was connected with the binding post P_0. The distance between the upper surface of the plate *P* and the free surface of the liquid was 20 mm. The glass cylinder was immersed in paraffin oil, contained in a Dewar beaker. The oil was heated electrically by means of a resistance *W* and efficient circulation was obtained with the stirrer *L*. The temperature of the oil was determined with the aid of a thermometer graduated into 0.2°C. The difference between the temperature of the liquid in the tube and that of the oil was measured with a thermoelement.

The amplitudes of the rotor were measured with the aid of mirror, scale and telescope. In order to avoid corrections for large deviations, a circular scale of 648 mm diameter was used in the center of which the rotor was placed. The case (*B*) prevented air currents from disturbing the movements of the rotor. A glass window at the bottom of the case permitted observation of the oscillations of the rotor. The time of oscillation in air was 25.8 sec.

Electrical connections

A source of direct current was connected to the terminals of a potentiometer, from which the required voltage was obtained.

Alternating current was obtained from the secondary of a transformer. The terminals of the primary were connected to an inductor alternator, the voltage of which could be controlled. The frequency was 1200 cycles per sec. The voltage was measured by means of a hot-wire voltmeter.

[5] W. Gerlach, *Materie, Elektrizität, Energie*, Dresden (1926), p. 40.

Device for filling and emptying the tube

The substances investigated, *e.g.*, *p*-azoxyphenetol, are solid at room temperature. *p*-azoxyphenetol melts and passes into the mesomorphic state at a temperature of 137°C. The liquid becomes isotropic at 167.5°C. Even the mesomorphic liquid has a considerable vapor tension. In order to fill and empty the tube and to clean it easily without having to change its position, operations which are often carried out, a special device was designed.

The size of the rotor and the disk

It is not easy to find a suitable size for the rotor. The time of oscillation should not be less than about 10 seconds, since it is otherwise difficult to take the readings. The time of oscillation can be increased by increasing the moment of inertia by a weight. The diameter of this weight is limited by that of the tube, which must be cylindrical. The weight of the whole rotor must not exceed a value corresponding to the elastic limit of the wire. Finally the logarithmic decrement must possess an adequate value.

Several different types of rotors were designed and constructed. In order to check the constancy of the torsion modulus, the time of oscillation was determined after every experiment.

The Viscosity of an Aeolotropic Liquid Depends on the Magnitude of the Shearing Stress

A comparison of the values obtained by using our apparatus with those obtained by the capillary method may be of interest.

The relation between the logarithmic decrement λ, the viscosity η and the density ρ of a liquid can be expressed by an equation, derived by Meyer[6] and used by Fawsitt[7] and others for the determination of the viscosity of melts. The equation is,

$$\lambda-\lambda_0=C_1(\rho\eta)^{\frac{1}{2}}+C_2\rho\eta+C_3\eta,$$

where λ_0 is the logarithmic decrement in air, and

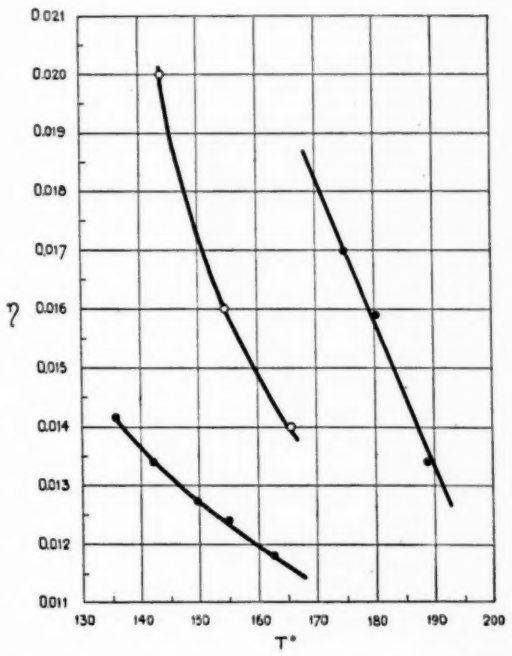

FIG. 3. Influence of the experimental arrangement on the viscosity. Closed circles, values obtained by Eichwald and published by Schenck.[8] Open circles, values obtained with the aid of the rotor method.

C_1, C_2 and C_3 are constants. As will be shown below this equation is not strictly applicable to the experimental arrangement in question. An investigation has shown that the equation, after determination of the constants C_i can be used as an interpolation formula.

The results of some measurements on *p*-azoxyanisol are recorded in Fig. 3. The values on the viscosity of the isotropic liquid are identical with those obtained by the capillary method. This, however, is not the case for the liquid in the aeolotropic state. The values calculated from experiments with the rotor method are greater than those obtained by Ostwald's method. The reason for this is that a more complete orientation of the particles or a more complete deformation of the liquid is effected when the last method is used. The result is of interest since it shows that the value of the viscosity is a function of the shearing stress which in turn is dependent on the experimental arrangement used and on the structure formed in the liquid.

[6] O. E. Meyer, *Innere Reibung*, Poggendorfs Ann. **113**, 71 (1861).

[7] C. H. Fawsitt, *On the Determination of Viscosity at high Temperatures*, Proc. Roy. Soc. **A80**, 290 (1908).

[8] R. Schenck, *Kristallinische Flüssigkeiten*, (1905) Leipzig.

The Influence of an Electric Field on Isotropic Liquids

With the aid of the arrangement described some preliminary experiments were made in order to ascertain if ordinary isotropic liquids are influenced by an electric field. Table I shows some results with xylol and direct voltage. The distance between the fixed plate and the disk was 2.0 mm. In the table, V the voltage is in volts, T the temperature and λ the decrement.

If the rotor is the positive terminal a decrease of decrement is found, if it is negative an increase results. The latter effect is more marked. The experiment was repeated with alternating voltage. Some values are given in Table II.

Table I. *Influence of an electric field on xylol.* (Time of oscillation for $V=0$, 26.0 sec.)

V	T	λ
0	19.2°	0.0270
+220	"	0.0261
−220	"	0.0290

Table II. *Influence of an electric field on xylol.* (Time of oscillation 26.0 sec., $V=0$).

V	T	λ
0	20.2	0.0261
150	"	0.0264
0	"	0.0267
150	"	0.0264

Table III. *Influence of an electric field on isotropic p-azoxyphenetol.* Distance between plates, 2.50 mm. Time of oscillation for $V=0$, 26.2 seconds. The rotor was the negative terminal. T is the temperature in °C, V the voltage in volts.

T	V/cm	λ
179.1	0	0.068
180.0	160	0.062
180.0	320	0.053
179.8	0	0.067
179.7	640	0.045

Table IV. *The change of decrement by an electric field.* Isotropic *p*-azoxyphenetol, alternating voltage.

T	V/cm	λ
174.0	0	0.074
174.0	400	0.075
174.0	0	0.072
174.1	600	0.073
174.2	0	0.075

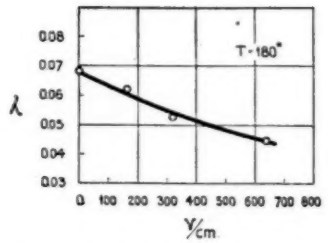

Fig. 4. Dependence of the field on the logarithmic decrement (isotropic liquid; direct voltage).

In this case no change in decrement can be found. Similar results were obtained with other liquids, for instance with benzene. Some values from experiments on azoxyphenetol in the isotropic state are recorded in Table III, and diagram 4.

The decrement is decreased with the voltage. The decrease was less when the rotor was the positive terminal.

The results of some experiments with alternating voltage are presented in Table IV.

These measurements show that the decrement is independent of the voltage of the alternating current.

The effect found with direct voltage can probably be interpreted as due to an electrolytic action. *p*-azoxyphenetol possesses a conductivity of the order of magnitude 10^{-8} ohm^{-1}cm^{-1}. The surface layer of the oscillating disk was changed. A change of the viscosity of the liquid, i.e., a volume effect seems to be excluded at least in

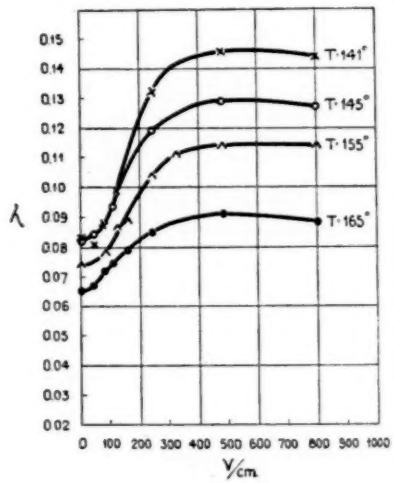

Fig. 5. Dependence of an electric field on the decrement (direct voltage).

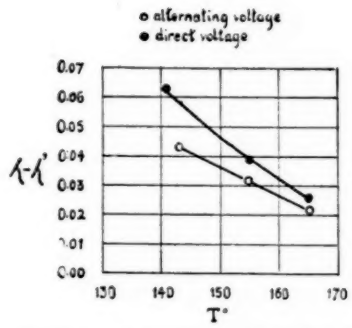

FIG. 6. Dependence of temperature on the decrement.

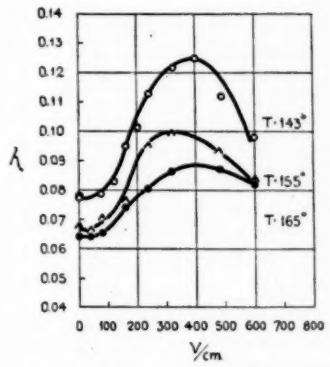

FIG. 7. Dependence of an electric field on the decrement (alternating voltage).

most cases. The conclusions regarding the orientation of the molecules that can be drawn from Langevin's theory for the Kerr effect show that even in most liquids with a marked dipole moment this orientation is insignificant.

THE INFLUENCE OF THE ELECTRIC FIELD ON THE AEOLOTROPIC LIQUID

Some results obtained from measurements of the change of the logarithmic decrement in an electric field (direct voltage) are given in Table V. In Table V, T the temperature is in °C, V/cm the intensity of the field in volts per cm, λ the decrement and ρ the specific gravity of the liquid.

TABLE V. *Change of decrement in an electric field.* (*p*-azoxyphenetol) direct voltage, time of oscillation 26.2 sec. ($V=0$).

T	V/cm	λ	ρ	$\lambda-\lambda^1$
165.0	0	0.065	1.070	0
165.0	40	0.067		0.002
165.0	160	0.079		0.014
165.6	80	0.072		0.007
164.7	120	0.074		0.009
164.3	240	0.085		0.020
164.7	480	0.091		0.026
164.7	800	0.088		0.023
155.0	0	0.075	1.082	0
154.2	160	0.089		0.014
154.3	320	0.111		0.036
154.6	80	0.077		0.002
154.6	120	0.087		0.012
154.5	240	0.104		0.029
154.7	480	0.114		0.039
155.0	800	0.114		0.039
145.1	40	0.084	1.092	
146.2	104	0.094		
145.4	240	0.119		
145.3	480	0.129		
145.4	800	0.127		
141.1	0	0.083	1.096	0
141.4	40	0.081		−0.002
141.4	80	0.088		0.005
141.4	120	0.098		0.015
141.4	240	0.128		0.045
141.4	480	0.146		0.063
141.4	800	0.140		0.057
141.6	0	0.080		

TABLE VI. *Influence of an electric field (alternating voltage) on decrement in p-azoxyphenetol.* Distance between plates 2.5 mm; time of oscillation 26.0 sec. ($V=0$).

T	V/cm	λ	ρ	$\lambda-\lambda^1$
143.7	0	0.078	1.094	0
143.2	0	0.079		0.00
143.2	80	0.079		0.001
143.2	120	0.083		0.005
143.0	160	0.095		0.017
143.0	200	0.101		0.023
143.5	0	0.077		−0.001
143.5	240	0.113		0.035
143.3	320	0.121		0.043
143.3	0	0.079		0
143.3	400	0.125		0.046
143.3	480	0.112		0.033
143.3	600	0.098		0.020
143.3	0	0.079		0.000
154.4	0	0.068	1.082	0
154.9	40	0.067		−0.001
154.9	80	0.071		0.003
154.9	160	0.077		0.009
154.6	0	0.069		0.001
154.6	240	0.096		0.028
154.6	320	0.100		0.032
154.5	0	0.068		0.000
154.5	480	0.094		0.026
154.5	600	0.083		0.015
154.7	0	0.068		0.000
165.5	0	—	1.070	—
165.5	40	0.064		0.000
165.0	80	0.065		0.001
165.2	160	0.074		0.010
165.2	0	0.064		0
165.2	240	0.080		0.016
165.4	320	0.086		0.022
165.4	480	0.087		0.023
165.5	600	0.082		0.018
165.5	0	0.064		0.000

The rotor was the negative terminal. The effect was independent of the direction of the field. As Fig. 5 shows, the decrement is independent of the voltage up to about 100 volts per cm. At higher voltages the decrement rises and reaches a value of saturation at about 500 volts per cm. The action is most pronounced at low temperatures. The temperature variation of the effect is shown in Fig. 6.

Similar experiments were made with alternating voltage. The results are given in Table VI.

The symbols are the same as in Table V. Fig. 7 shows the change of the decrement with the intensity of the field. In Fig. 6 the influence of the temperature is shown. The change increases with the field, attains a maximum and decreases again. The effect is greatest at low temperatures.

Similar results were obtained with *p*-azoxyanisol, although the effect was smaller.

Theory

The problem of a disk oscillating in a viscous medium has been treated by Coulomb,[9] Maxwell[10] and Meyer.[6] Coulomb and Meyer discuss the case of a disk oscillating in a very large volume, while Maxwell assumes that the disk is placed in the middle of two fixed plates. For the most part the method has been used by these authors to study the viscosity of air.

A numerical lower limit for the change of viscosity in an electric field can be obtained if we assume that the change is produced in the whole liquid. A value of η_e is obtained from equation (p. 5) developed from Meyer's theory. The values obtained using such a theory are of course smaller than the actual ones.

Neither theory can be applied to the experimental arrangement used by us. However, it is possible to generalize Maxwell's discussion and obtain a relation between decrement and viscosity.

Consider a layer of liquid of the height dy at the distance y from the fixed plate (Fig. 8) and an element of volume at the distance r from the axis and with an azimuth θ. If the viscosity of the liquid between the disk and the plate be η, and

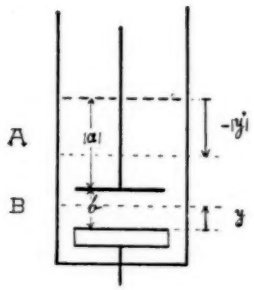

Fig. 8.

the tangential velocity of the element v, the force which is acting on the lower surface of the volume element is $\eta\partial v/\partial y$ or $\eta r\partial^2\theta/\partial t\partial y$. The force acting on the upper surface of the layer is

$$\eta r\partial^2\theta/\partial t\partial y+\eta r(\partial^3\theta/\partial y^2\partial t)dy.$$

The resultant force acting on the element is $\eta r\partial^3\theta/\partial y^2\partial t$ and the equation of motion of the element is expressed by

$$\rho\partial^2\theta/\partial t^2=\eta\partial^3\theta/\partial y^2\partial t\,; \qquad \text{(B)}$$

For a layer between the disk and the surface of the liquid at the distance y' from the surface at the liquid we get

$$\rho\partial^2\theta'/\partial t^2=\eta'\partial^3\theta'/\partial y'^2\partial t, \qquad \text{(A)}$$

where η' is the viscosity and θ' the azimuth of the volume element. I have assumed two different viscosities η and η'. As a matter of fact the viscosity in the aeolotropic liquid is not a constant but varies during an oscillation and with y and y', respectively, since it depends on $\partial v/\partial y$. Even in the same layer the viscosity decreases with increasing r, and it is only in the interest of simplicity that I have made a provisional assumption of only two different viscosities η and η'.

The equations A and B show that the motion is independent of r. The boundary conditions are:

$$\begin{cases}\partial^2\theta'/\partial y'\partial t=0\\ y'=0\end{cases}, \quad \begin{cases}y=0\\ \theta=0\end{cases}, \quad \begin{cases}y=b\\ y'=-a,\\ \theta=\theta'.\end{cases}$$

The equation of movement of the rotor is expressed by

$$I\left[\frac{\partial^2\theta}{\partial t^2}+2h\frac{d\theta}{\partial t}+\Omega^2\theta\right]+A\eta\frac{\partial^2\theta}{\partial y\partial t}-A\eta'\frac{\partial^2\theta'}{\partial y'\partial t}=0,$$

[9] Ch. Coulomb, Mem. de l'Inst. **4**, 431 (1822).
[10] J. C. Maxwell, Proc. Roy. Soc. **A156**, 259 (1866).

where I is the movement of inertia, $A=\pi r^4/2$ and the second term is due to the damping action of the air on the upper part of the rotor. Let us try the solution

$$\theta'=e^{(-l+i\omega)t+\alpha'}\cos u'y'=e^{\alpha t+\alpha'}\cos u'y';$$

$$\theta=e^{\alpha t}\sin uy;$$

where u, u' are complex quantities. From (A) and (B) we obtain

$$\rho\alpha=-\eta' u'^2; \quad \rho\alpha=-\eta u^2;$$

The conditions for $y=b$; and $y'=-a$ give $e^{\alpha'}\cos u'a=\sin ub$;

$$(I/A)(\alpha^2+2\alpha h+\Omega^2)+\eta\alpha u\operatorname{ctg} ub-\eta'\alpha u'\operatorname{tg} u'a=0,$$

$$\frac{I}{\rho A}\left(1+\frac{2h}{\alpha}+\frac{\Omega^2}{\alpha^2}\right)-\frac{1}{u}\operatorname{ctg} ub+\frac{1}{u'}\operatorname{tg} u'a=0.$$

The quantities I, A, h, Ω, ρ, b, a are all known. The equation may be written

$$\phi[\alpha, \eta, \eta']=0$$

or if the real and imaginary parts are separated and if $\alpha=-l+i\omega$ where l is the damping factor and ω the frequency

$$\phi_r[l, \omega, \eta, \eta']=0,$$

$$\phi_i[l, \omega, \eta, \eta']=0,$$

$$\lambda=\log^{10}\theta_n/\theta_{n+1}=l\log^{10}e.$$

The quantities l and ω are determined by experiment. We can obtain values on η and η'. It can be shown that a numerical calculation can be carried out at least if the difference $\eta-\eta'$ is not great.*

In the case of an electrical field we obtain the analogous equations

$$\phi_r[l_e, \omega_e, \eta_e, \eta_e']=0,$$

$$\phi_i[l_e, \omega_e, \eta_e, \eta_e']=0,$$

where η_e is the viscosity under the influence of the field, η_e' the viscosity above the disk, l_e the damping factor, and ω_e the frequency at the oscillation. Since $\eta_e'=\eta'$ it is not necessary to determine ω_e.

* The author is indebted to Dr. E. Hogner and to Mr. N. Larsson for some suggestions as regards these calculations.

Although it is possible to calculate η, η' and η_e from the equations, we refrain from giving any numerical values. The theoretical assumptions are doubtful. The problem is much more complicated than we have assumed. Furthermore, the aeolotropic liquids possess a special structure, which is distorted by the oscillations of the disk. As another argument may be mentioned that Newton's assumptions for the tensor of viscosity is not valid for aeolotropic liquids. Oseen[11] and Anzelius[12] have suggested still other possibilities.

Change of electrical conductivity under shearing stress

As regards the cause of this electrical viscosity effect it is not difficult to explain it as resulting from an orientation or a distortion of the swarms. This hypothesis has been verified by comparison with the results obtained from measurements of the electrical conductivity and dielectric constant.

The commutator method used by The Svedberg[1] for determinations of the conductivity of comparatively concentrated electrolyte solutions fails in the case of pure liquids, which are characterized by a small conductivity. However, if special precautions are observed, the ordinary bridge method can be adapted even to the measurement of the high resistances in question. An earthing device analogous to that designed by Wagner[13] was used and certain of the resistances were shielded. Voltage of a frequency of about 1000 cycles per sec. was obtained from an alternator, which allowed the voltage to be varied between the desired limits. A band-pass filter served to suppress the harmonies. In order to prevent a too assymetrical distribution of the earth-admittances an input transformer was used. As null indicator an impedance matching transformer connected to a two-stage amplifier and a telephone was used.[14]

Since disturbances due to the capacity to earth are possible, the arrangement was tested by the following method. A resistance was substituted for the cell and the voltage was varied. The re-

[11] C. W. Oseen, Trans. Faraday Soc. **29**, 895 (1933).
[12] A. Anzelius, *Über die Bewegung der anisotropen Flüssigkeiten*, Diss. Upsala 1931.
[13] K. W. Wagner, Elektrotech. Zeits. **32**, 1001 (1931).
[14] The author is indebted to Professor L. Ramberg for the loan of some instruments.

TABLE VII. *Dependence of conductivity on the field,* (*p*-azoxyphenetol; $T=144^{5}$).

E (volts per cm)	$\kappa\times10^{8}$ ($\text{ohm}^{-1}\ \text{cm}^{-1}$)
6.8	4.0
19	4.0
65	4.1
157	4.6
195	4.7

sistance was found to be independent of the voltage.

Since the method was to be used only for the purpose of analysis the cell constant was not determined, but the specific conductivity was calculated from the diameter and distance of the plates neglecting boundary corrections. The dependence of the conductivity on the field was determined (Table VII). The conductivity increases with the intensity. It is evident that the critical limit is about 70 volts per cm. In order to eliminate this influence a low voltage was used.

When the rotor was at rest a conductivity $\kappa=4.5\times10^{-8}$ $\text{ohm}^{-1}\ \text{cm}^{-1}$ was obtained. With oscillation, i.e., under shearing stress κ was found to be 4.2×10^{-8} at a distance between the plates 1.02 mm, the voltage being 0.67 volts, corresponding to 6.6 volts per cm. The temperature was 144°C. In other experiments the decrease of conductivity varied between $0.0-0.2\times10^{-8}$ $\text{ohm}^{-1}\ \text{cm}^{-1}$.

The measurements have been of a preliminary nature and are not yet completed. A comparison with the results obtained by Svedberg[1] shows that in the absence of an electric field the swarms in the liquid under shearing stress display a tendency to arrange themselves with their axes parallel to the plates. In an electric field an orientation is effected with the axis at right angles to the plates.

It is evident that layers consisting of swarms orientated in this way must tend to increase the viscosity.

It has been supposed that the axis of the swarms in a nematic liquid tends towards a transversal position in an electric field for the following reason. In a magnetic field a decrease of the dielectric constant has been observed suggesting that $\epsilon_p<\epsilon_e$, where ϵ_p is the dielectric constant parallel to the axis of the swarm.

In an electric field the stable equilibrium corresponding to a minimum of potential energy would thus involve a transversal orientation of the axes of the swarms.

My results militate against the theory of transversal orientation, but agree closely with those obtained by Kast,[15] who has found by x-ray investigations that the axis of the swarm inclines towards a longitudinal position in an electric field. In order to explain this curious phenomenon Ornstein[16] has suggested that the swarms have a fixed dipole moment in the direction of the axis, which only slightly affects the value of the dielectric constant.

In view of the chemical formula for *p*-azoxyphenetol, it seems unlikely that a great dipole moment should exist in a direction parallel with the axis of the molecule. I refer to my alternative hypothesis, first evolved in 1918 concerning the orientation of the swarms in a nematic liquid[2] p. 183 and p. 201.

By microscopic observations on *p*-azoxyphenetol and *p*-azoxyanisol in an homogeneous electric field, I have found small spherical particles or drops, which move about in the liquid. The phenomenon is probably due to the formation of space charges. The shearing stress produced by the movement causes the orientation of the swarms. That such "mechanical" orientation is possible is clearly shown by the experiment described above. The movement of the rotor causes the axis of swarms to become parallel with the plates.

[15] W. Kast, *Anisotrope Flüssigkeiten im elektrischen Felde*, Zeits. f. Physik **71**, 39 (1931).
[16] L. S. Ornstein, Zeits. f. Krist. **79**, 331 (1931).

The Motion of a Viscous Fluid Under a Surface Load

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A formal solution is given for the motion of a highly viscous fluid when a symmetrical pressure is applied at the surface. This is applied to the subsidence of a cylindrical body of constant thickness and to the recovery of the fluid after removal of a load. Applying the latter case to the plastic recoil of the earth after the disappearance of the Pleistocene ice sheets, it is found that the geological data imply a kinematic viscosity of the order of 3×10^{21} c.g.s. units.

INTRODUCTION

OBSERVATIONS on the elevated and tilted shore lines of the glaciated tracts of Europe and North America have shown that during and following the disappearance of the Pleistocene ice sheets the earth returned to a configuration of equilibrium by delayed plastic flow as well as by immediate elastic recovery. The progress of this recovery has been dated by means of varved glacial clays and F. Nansen[1] has constructed curves illustrating the uplift of the Fennoscandian region from 16,000 B.C. to the present time. This suggests the possibility of determining the effective viscosity of the earth's outer shells under forces of long duration.

In the present paper we shall neglect the curvature of the earth and treat the problem of the motion of a semi-infinite, incompressible, viscous fluid under the action of a radially symmetrical pressure applied at the free surface. Since, in the case of the earth, we are dealing with extremely small accelerations and very high viscosity, we may neglect the inertial terms in the equations of motion in comparison with those arising from viscous forces. We shall first treat the case of an arbitrary symmetrical impressed pressure and then apply the results to two special cases, (1) a constant load of radius r_0 applied at $t=0$, and (2) recovery after the removal of an arbitrary symmetrical load.

1. FORMULATION OF THE PROBLEM

Neglecting the terms arising from the acceleration, the equations of motion of a fluid of viscosity η and density ρ in a gravitational field g are;—

$$\eta\nabla^2 V=\text{grad } p-(0,0,\rho g), \tag{1.1}$$

$$\text{div } V=0, \tag{1.2}$$

where the positive z axis has been taken as directed downward. Transforming to cylindrical coordinates (r, z, ϕ), assuming radial symmetry, and setting $\bar{p}=p-\rho gz$, these become

$$\partial/r\partial r(r\partial V_r/\partial r)-V_r/r^2+\partial^2 V_r/dz^2=\partial\bar{p}/\eta\partial r, \tag{1.11}$$

$$\partial/r\partial r(r\partial V_z/\partial r)+\partial^2 V_z/\partial r^2=\partial\bar{p}/\eta\partial z, \tag{1.12}$$

$$\partial/r\partial r(rV_r)+\partial V_z/\partial z=0. \tag{1.21}$$

The components of stress in which we are interested are

$$p_{zz}=-(\bar{p}+\rho gz)+2\eta\partial V_z/\partial z, \tag{1.31}$$

$$p_{rz}=\eta(\partial V_r/\partial z+\partial V_z/\partial r). \tag{1.32}$$

The boundary conditions are that on the free surface p_{rz} shall vanish and p_{zz} shall equal the applied stress, and at infinity the stresses and velocities shall vanish.

Let the equation of the free surface be $z=\zeta(r, t)$ and take the undisturbed surface as the plane $z=0$. If we assume that ζ remains small in comparison with other distances entering into the problem, such as the radius of the applied load, we may replace the value of $\partial V_z/\partial z$ at $z=\zeta$ by its value at $z=0$, and similarly with all the other quantities appearing in (1.31) and (1.32) except ρgz.[2] Calling the applied pressure $-\sigma(r, t)$, the boundary conditions become

$$\bar{p}(r,0,t)+\rho g\zeta(r,t)-2\eta(\partial V_z/\partial z)(r,0,t)=\sigma(r,t), \tag{1.41}$$

$$(\partial V_r/\partial z+\partial V_z/\partial r)_{z=0}=0 \tag{1.42}$$

and

$$\partial\zeta/\partial t=V_z(r,0,t). \tag{1.43}$$

2. GENERAL SOLUTION FOR ARBITRARY IMPRESSED LOAD

Setting $V_r=R_1(r)Z_1(z)$, $V_z=R_2(r)Z_2(z)$, $\bar{p}=R_3(r)Z_3(z)$ in (1.11), (1.12), and (1.21), and

[1] F. Nansen, *The Earth's Crust, Its Surface Forms and Isostatic Adjustment* (1928), Oslo.

[2] This is the sort of approximation commonly made in treating waves on the surface of a fluid. Cf., H. Lamb, *Hydrodynamics*, fifth edition, Chaps. IX. & XI.

separating variables, we have the Bessel equations,

$$d/rdr(rdR_1/dr)-R_1/r^2+\lambda^2R_1=0, \quad (2.11)$$

$$d/rdr(rdR_2/dr)+\lambda^2R_2=0 \quad (2.12)$$

and $$R_3=\text{const.}\times R_2. \quad (2.13)$$

The appropriate solutions are $R_1=J_1(\lambda r)$, $R_2=R_3=J_0(\lambda r)$, where we have included the constant factor in R_3 in the z factor. The z equations are

$$d^2Z_1/dz^2-\lambda^2Z_1=-\lambda Z_3/\eta, \quad (2.21)$$

$$d^2Z_2/dz^2-\lambda^2Z_2=dZ_3/\eta dz, \quad (2.22)$$

$$\lambda Z_1+dZ_2/dz=0. \quad (2.23)$$

Eliminating Z_1 and Z_3, we have the fourth order equation for Z_2

$$d^4Z_2/dz^4-2\lambda^2d^2Z/dz^2+\lambda^4Z_2=0. \quad (2.3)$$

The solutions of this equation are $e^{\pm\lambda z}$, $ze^{\pm\lambda z}$ of which only those with negative exponents are appropriate to the present problem. The solutions of the set (2.21), (2.22), (2.23) are then,

$$Z_2=e^{-\lambda z}(A+Bz), \quad (2.41)$$

$$Z_1=e^{-\lambda z}(A-B/\lambda+Bz), \quad (2.42)$$

$$Z_3=2\eta Be^{-\lambda z}. \quad (2.43)$$

In order to satisfy the boundary condition (1.42) we have $B=\lambda A$.[3] We must now satisfy (1.41) with functions of the form

$$V_r=z\int_0^\infty A(\lambda)e^{-\lambda z}J_1(\lambda r)\lambda d\lambda, \quad (2.51)$$

$$V_z=\int_0^\infty A(\lambda)e^{-\lambda z}J_0(\lambda r)(1+\lambda z)d\lambda, \quad (2.52)$$

$$\bar{p}=2\eta\int_0^\infty A(\lambda)e^{-\lambda z}J_0(\lambda r)\lambda d\lambda. \quad (2.53)$$

From (2.51) $\partial V_z/\partial z=0$ at $z=0$, hence (1.41) becomes

$$2\eta\int_0^\infty A(\lambda)J_0(\lambda r)\lambda d\lambda+\rho g\zeta=\sigma(r,t). \quad (2.61)$$

A will evidently have to be a function of the time in order to satisfy this equation, hence we may differentiate with respect to t and use (1.43). Then

$$\int_0^\infty J_0(\lambda r)\{2\eta\partial A/\partial t+\rho gA/\lambda\}\lambda d\lambda=\partial\sigma/\partial t. \quad (2.62)$$

Application of the Fourier-Bessel inversion formula yields a first order differential equation for A as a function of t.

$$2\eta\partial A/\partial t+\rho gA/\lambda=\int_0^\infty(\partial\sigma/\partial t)J_0(\lambda r)rdr. \quad (2.7)$$

The solution is[4]

$$A=K(\lambda)e^{-\rho gt/2\eta\lambda}+\frac{1}{2\eta}e^{-\rho gt/2\eta\lambda}\int_0^t\int_0^\infty\frac{\partial\sigma}{\partial t}e^{\rho gt/2\eta\lambda}J_0(\lambda r)rdrdt, \quad (2.81)$$

where $K(\lambda)$ must be determined from the initial conditions. Integrating the second term by parts with respect to t

$$\int_0^t\frac{\partial\sigma}{\partial t}e^{\rho gt/2\eta\lambda}dt=\sigma e^{\rho gt/2\eta\lambda}-\sigma_0-\frac{\rho g}{2\eta\lambda}\int_0^t\sigma e^{\rho gt/2\eta\lambda}dt.$$

Hence

$$A=K(\lambda)e^{-\rho gt/2\eta\lambda}+\frac{1}{2\eta}\int_0^\infty\sigma J_0(\lambda r)rdr-\frac{1}{2\eta}e^{-\rho gt/2\eta\lambda}\int_0^\infty\sigma_0J_0(\lambda r)rdr-\frac{\rho g}{4\eta^2\lambda}e^{-\rho gt/2\eta\lambda}\int_0^t\int_0^\infty\sigma e^{\rho gt/2\eta\lambda}J_0(\lambda r)rdrdt. \quad (2.82)$$

This expression, with Eqs. (2.51), (2.52), (2.53) is the formal solution of the problem.

3. Subsidence of a Cylindrical Body

If we suppose that the fluid is initially at rest and that at $t=0$ a uniform circular load of radius r_0 is placed on the surface,

$$\sigma(r,t)=\begin{cases}0; & r>r_0\\ 0; & t\leq 0\\ \sigma=\text{const}; & r<r_0,\ t>0.\end{cases} \quad (3.1)$$

Then $K(\lambda)=0$, and by using

$$\int_0^{r_0}J_0(\lambda r)rdr=(r_0/\lambda)J_1(\lambda r)$$

$$A=(\sigma r_0/2\eta\lambda)e^{-\rho gt/2\eta\lambda}J_1(\lambda r_0). \quad (3.2)$$

By substituting in (2.51), (2.52) and (2.53),

$$V_r=(z\sigma r_0/2\eta)\int_0^\infty e^{-\rho gt/2\eta\lambda-\lambda z}\times J_1(\lambda r_0)J_1(\lambda r)d\lambda, \quad (3.31)$$

[3] Note that this is the same relationship that we would get if instead of the vanishing of p_{rz} at $z=0$ we took as a boundary condition that $V_r=0$ at $z=0$. The latter is the condition we would have if we assumed that on the surface of the fluid there lay a solid crust capable of resisting tangential deformation, but opposing a negligible resistance to vertical deformation.

[4] E. L. Ince, *Ordinary Differential Equations*, p. 21.

$$V_z=(\sigma r_0/2\eta)\int_0^\infty e^{-\rho g t/2\eta\lambda-\lambda z}\times J_1(\lambda r_0)J_0(\lambda r)((1+\lambda z)/\lambda)d\lambda, \quad (3.32)$$

$$\bar{p}=\sigma r_0\int_0^\infty e^{-\rho g t/2\eta\lambda-\lambda z}J_1(\lambda r_0)J_0(\lambda r)d\lambda, \quad (3.33)$$

$$\zeta=\int_0^t V_z(r,0,t)dt=(\sigma r_0/\rho g)\int_0^\infty(1-e^{-\rho g t/2\eta\lambda})\times J_1(\lambda r_0)J_0(\lambda r)d\lambda. \quad (3.34)$$

We may note as a check that as $t\to\infty$

$$\zeta\to(\sigma r_0/\rho g)\int_0^\infty J_1(\lambda r_0)J_0(\lambda r)d\lambda = \begin{cases} 0; & r>r_0 \\ \sigma/\rho g; & r<r_0, \end{cases} \quad (3.35)$$

so that the system approaches the configuration of hydrostatic equilibrium asymptotically as it should.

It does not appear to be possible to express the above integrals in closed form. They may be put in dimensionless form for numerical or mechanical integration by setting

$$\tau=\rho g r_0 t/2\eta, \quad x=r/r_0, \quad y=z/r_0,$$
$$K=\lambda r_0, \quad v_r=2\eta V_r/\sigma r_0, \quad v_z=2\eta V_z/\sigma r_0,$$
$$\pi=\bar{p}/\sigma, \quad \mu=\rho g\zeta/\sigma.$$

Then

$$v_r=y\int_0^\infty e^{-\tau/K-Ky}J_1(K)J_1(Kx)dK, \quad (3.41)$$

$$v_z=\int_0^\infty e^{-\tau/K-Ky}J_1(K)\times J_0(Kx)((1+Ky)/K)dK, \quad (3.42)$$

$$\pi=\int_0^\infty e^{-\tau/K-Ky}J_1(K)J_0(Kx)dK, \quad (3.43)$$

$$\mu=\int_0^\infty(1-e^{-\tau/K})J_1(K)J_0(Kx)dK. \quad (3.44)$$

4. Recovery after Removal of Load

Setting the applied pressure, σ, equal to zero over the whole surface in (2.82) we have

$$A=K(\lambda)e^{-\rho g t/2\eta\lambda}.$$

$K(\lambda)$ can then be determined either from the initial velocity at the surface or from the initial configuration of the surface. From (2.52)

$$V_z(r,0,0)=\int_0^\infty K(\lambda)J_0(\lambda r)d\lambda. \quad (4.11)$$

Hence, by inversion,

$$K(\lambda)=\lambda\int_0^\infty V_z(r,0,0)J_0(\lambda r)rdr. \quad (4.12)$$

We also have

$$\zeta=\zeta(r,0)+\int_0^t V_z(r,0,0)dt. =\zeta(r,0)+(2\eta/\rho g)\int_0^\infty K(\lambda)(1-e^{-\rho g t/2\eta\lambda})\times J_0(\lambda r)\lambda d\lambda. \quad (4.21)$$

As t becomes infinite, ζ must approach zero, therefore

$$\zeta(r,0)=-(2\eta/\rho g)\int_0^\infty K(\lambda)J_0(\lambda r)\lambda d\lambda \quad (4.22)$$

or, inverting,

$$K(\lambda)=-(\rho g/2\eta)\int_0^\infty\zeta(r,0)J_0(\lambda r)rdr. \quad (4.23)$$

Thus the subsequent motion is completely determined if we know either $\zeta(r,0)$ or $V_z(r,0,0)$.

5. Application to Post-Glacial Uplift of Fennoscandia

It would, of course, be impossible to calculate the motion of the earth throughout the history of the retreat of a continental ice sheet, since both the radius and the thickness varied with time in an irregular and, in the case of the thickness, an unknown manner. Moreover, an important part of the uplift (estimated as one-sixth to one-quarter of the total) was due not to plastic flow but to elastic recovery. However, the results of the last section show that we may treat the part of the uplift which took place after the complete disappearance of the ice without any knowledge of how fast it retreated or how its thickness varied provided we know the rate of uplift at all distances from the center, or the configuration of the surface, at some time subsequent to the completion of the melting. During this part of the motion we do not need to consider the elastic component, since that would keep pace with the decrease in the load and would be complete when the ice had disappeared.

Nansen's curves (Figs. 1 and 2) give the amount and rate of uplift at a point in Ångermanland near the center of the Fennoscandian glaciated region and at Oslo, about 500 km distant. In order to use this data it will be necessary to assume a reasonable form for either $\zeta(r,0)$, the initial configuration of the surface, or $V_2(r,0,0)$, the initial rate of uplift, and fit the assumed function to the values given for these two points. It is reasonable to suppose that $V_z(r,0,0)$ will

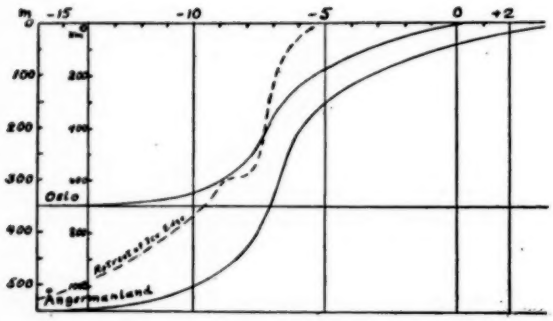

FIG. 1. Uplift of the Fennoscandian region. Abscissas are times in units of 1000 years B.C. and A.D. Ordinates (solid curves) are depths of the surface in meters below equilibrium level. Ordinates of the dotted curve give the radius of the ice cap in kilometers.

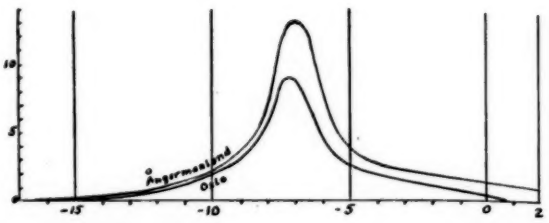

FIG. 2. Rate of uplift in meters per century. Abscissas in units of 1000 years.

have a maximum at the center and will decrease outward in a way that can be represented with sufficient accuracy by an exponential function. We shall suppose then that

$$V_z(r, 0, 0) = -ae^{-b^2r^2}, \tag{5.1}$$

using the square of r in the exponent rather than the first power in order to avoid having a cusp at the center. By substituting in (4.12),

$$K(\lambda) = -a\lambda \int_0^\infty e^{-b^2r^2} J_0(\lambda r) r dr$$

$$= -(a\lambda/2b^2)e^{-\lambda^2/4b^2}. \tag{5.2}$$

By using (4.21) and (4.22),

$$\zeta = (a\eta/\rho g b^2) \int_0^\infty e^{-\lambda^2/4b^2 - \rho g t/2\eta\lambda} J_0(\lambda r)\lambda^2 d\lambda. \tag{5.3}$$

At $r=0$, $t=0$

$$\zeta(0, 0) = (a\eta/\rho g b^2) \int_0^\infty e^{-\lambda^2/4b^2} \lambda^2 d\lambda = 2\sqrt{\pi}(\eta a b/\rho g).$$

The kinematic viscosity, $\nu = \eta/\rho$, is then given by

$$\nu = g\zeta(0, 0)/2\sqrt{\pi} ab. \tag{5.41}$$

Since we are at liberty, in applying the above theory, to take any time after the disappearance of the ice as the initial instant $t=0$, we may check roughly the validity of the assumption that $V_z(r, 0, 0)$ does not depart very widely from the form given in (5.1) by calculating ν from (5.41) for various initial instants and seeing that it remains of the same order of magnitude. If we express $\zeta(0, 0)$ in meters, a in meters per century, and b in reciprocal kilometers, ν is given in c.g.s. units by

$$\nu = 8.73 \times 10^{16} \zeta(0, 0)/ab. \tag{5.42}$$

$\zeta(0, 0)$ may then be read from the curve for Ångermanland in Fig. 1, a from that in Fig. 2, and b may be calculated from the curve for Oslo in Fig. 2 by setting $r = 500$ in (5.1). In Table I the values of these quantities are given for various times taken as the initial instant.

The initial configuration of the surface, corresponding to the assumed initial velocity (5.1), is given by

$$\zeta(r, 0) = (a\eta/\rho g b^2) \int_0^\infty e^{-\lambda^2/4b^2} J_0(\lambda r)\lambda^2 d\lambda \tag{5.51}$$

or

$$\zeta(r, 0)/\zeta(0, 0) = (1/2\sqrt{\pi}) \int_0^\infty e^{-\lambda^2/4} J_0(\lambda x)\lambda^2 d\lambda, \tag{5.52}$$

where $x = br$. Values of this quantity as a function of x are given in Table II. Taking the initial instant at 5000 B.C., and using $b = 1.27 \times 10^{-3}$ km^{-1}, the initial profile of the surface and rate of uplift are plotted in Fig. 3. A complete observed profile is not available to compare with the calculated curve in order to determine how closely the assumptions made fit the actual case, but it may be noted that Fig. 3 indicates a depression of the surface at 500 km radius of about 76 meters. This is to be compared with 85 meters at Oslo at 5000 B.C. as read from the curve of Fig. 1.

In comparing the figure given above for the earth's kinematic viscosity with experimentally determined viscosities of solid substances it should be noted that two quite distinct properties

TABLE I. *Values of the quantities entering in Eq. (5.42) for various times taken as the initial instant.*

$t=0$	a	$b \times 10^3$	$\zeta(0, 0)$	$\nu \times 10^{-21}$
5,000 B.C.	3.9	1.27±.07	147	2.6±0.2
4,000 "	2.7	1.19±.09	118	3.2±0.3
3,000 "	2.2	1.24±.11	94	3.0±0.4
2,000 "	1.8	1.25±.15	74	2.9±0.5

Mean value: $\nu = 2.9 \times 10^{21}$ cm^2 sec.$^{-1}$

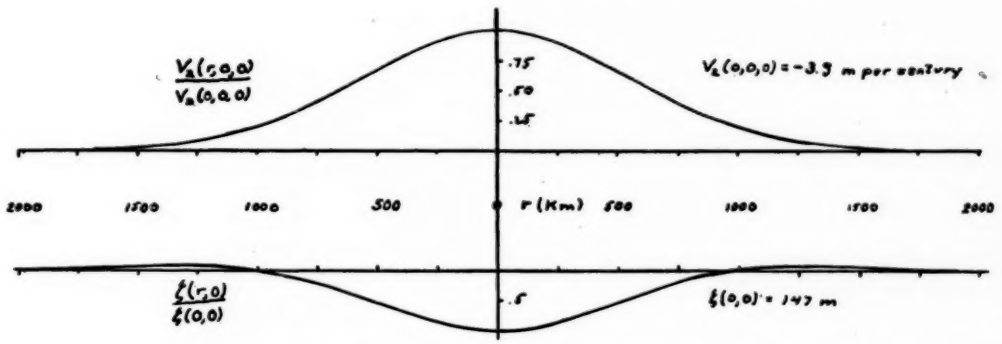

FIG. 3. Rate of uplift and surface profile at 5000 B.C. Vertical exaggeration of profile 1.7×10^3 times.

TABLE II.

x	$\zeta(r, 0)/\zeta(0, 0)$	x	$\zeta(r, 0)/\zeta(0, 0)$
0.0	+1.000	1.0	+0.155
0.2	+0.922	1.5	−0.076
0.4	+0.780	2.0	−0.068
0.6	+0.562	2.5	−0.033
0.8	+0.328		

TABLE III. *Values taken for the coefficient of viscosity of various substances.*

MATERIAL	TEMPERATURE	η (g. cm^{-1} sec.$^{-1}$)
Shoemakers wax	15°C	2×10^{8}
Asphalt	15	3×10^{10}
Ice	0	5×10^{12}
Glass	575	1×10^{13}
Lead	20	1×10^{16}
Calcite	18	1.5×10^{16}
Rocksalt	18	2×10^{18}

of matter are often included in the term.[5] One, which is better designated as inner friction, relates to the damping of elastic vibrations, the other relates to plastic flow. The coefficient of inner friction is of the order of 10^8 or 10^9 c.g.s. units for most metals and is higher for soft than for hard substances. The "true" coefficient of viscosity is more difficult to measure experimentally, different observers giving widely varying values,[6] and, in general, increases rapidly with the hardness of the substance. The figures given in Table III are taken from Gutenberg and Schlechtweg's paper. In view of the great increase of viscosity with the hardness of the material and the pressure, it is not surprising to find that for silicates under the enormous pressures within the earth the viscosity is as high as we have found here, even when the decrease of viscosity at high temperatures is taken into consideration.

R. W. van Bemmelen and H. P. Berlage[7] have recently made an estimate of the viscosity of the earth on the basis of post-glacial uplift using a method quite different from that followed hree. They find $\eta=1.3\times10^{20}$ which, since they assume a density of 3, is equivalent to $\nu=0.4\times10^{20}$. Their method makes use of special hypotheses concerning the structure and dynamics of the earth's crust and is only indirectly based on hydrodynamical theory. They also assume that the flow is confined to a layer 100 km thick and it is therefore to be expected that their value should be lower than that found by the present method. According to their theory ν varies as the cube of the assumed thickness of the layer, hence if it were taken to be 400 km, their figure would be comparable with ours.

In conclusion the author wishes to express his thanks to Professor L. B. Slichter, under whose guidance this work was done, for many helpful suggestions and criticisms. The graphical evaluation of the integral given in Table II was very kindly carried out by members of the Mathematics Laboratory of the Massachusetts Institute of Technology. Acknowledgment should also be made to Professor R. A. Daly's stimulating lectures on Pleistocene movements of the earth's crust, which originally suggested the problem.

[5] B. Gutenberg and H. S. Schlechtweg, *Viscosity and Inner Friction of Solid Bodies*, Physik. Zeits. **31**, 745 (1930).
[6] W. D. Kusnezow, Zeits. f. Physik. **51**, 239 (1928).
[7] R. W. van Bemmelen and H. P. Berlage, Gerl. Beit. z. Geophys. **43**, 19 (1934).

A Note on Viscosity as a Function of Volume and Temperature of Oils

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The viscosity-volume data of Kleinschmidt and Dow have been examined at various pressures and temperatures for lard, sperm and Pennsylvania medium oil. The viscosity-volume isotherms at 25°, 40° and 75°C are not identical for any of the oils studied, indicating that viscosity cannot be a function of the specific volume alone. The viscosity-volume curve for lard oil at 25° departs from the one at 75° by an amount sufficient to change the viscosity by a factor of 2.3 at a volume of 0.99, and by a factor of 3.2 at a volume of 0.93. Similar curves for Pennsylvania medium oil at the same temperatures are even more relatively displaced; the discrepancy in viscosity varies from a factor of 3.8 at a volume of 0.99 to 7.6 at 0.94. The three oils do not obey Batschinski's equation at atmospheric and higher pressures up to 4000 kg/cm².

COMPARATIVELY little is known of the physical properties of lubricating oils at high hydrostatic pressures. Among the non-thermodynamic properties of lubricants at high pressures, viscosity has been most extensively studied because of its significance for thick film lubrication. The experiments of Hyde[1] and, more recently, those of Hersey and Shore,[2] and Kleinschmidt,[3] have shown that the coefficient of viscosity of a mineral oil at ordinary temperatures increases by a factor of about 20 with an initial increase of pressure of 1000 kg/cm,[2] this increase being several times greater than that observed for pure liquids[4] or mixtures of liquids[5] through the same range of pressure. With the recent study of some of the thermodynamic properties of similar oils,[6] sufficient data are available for an examination of the viscosity of oils as a function of volume.

In addition to the practical usefulness of viscosity-volume data taken at various pressures and temperatures, there is theoretical interest in the functional relation between viscosity and volume. Consequently, this communication presents the viscosity-volume-temperature relations for three lubricating oils and includes a discussion of the theoretical relationship.

Data

Table I contains the log relative viscosities and volumes at various pressures and temperatures for lard, sperm and Pennsylvania medium oil, respectively, the data being taken from the papers of Kleinschmidt[3] and Dow.[6] The density of each oil at atmospheric pressure and 40°C is given in order that the specific volumes may be computed directly from the table of volumes by division. The log relative viscosities are expressed as $\log_{10} t/t_0$, t being the time of fall of a weight in a viscometer at a certain pressure and tempera-

TABLE I. *Relative viscosity and volume.*

Pressure kg/cm²	$\log_{10}$ Relative viscosity 25°	40°	75°	Volume 25°	40°	75°
			Lard oil $\rho_{40}=0.9009$ g/cm³			
1	0	$\bar{1}.770$	$\bar{1}.370$	0.9902	1.0000	1.0190
100	0.079	.845		.9844	.9936	
250	.183	.938	.500	.9763	.9850	1.0051
500	.345	0.082	.628	.9647	.9721	.9921
750	.499	.220	.742	.9550	.9615	.9800
1000	.642	.351	.855	.9461	.9523	.9697
1500	.920	.607	0.070	.9299	.9366	.9522
2000		.835	.262		.9229	.9374
2500		1.052	.441		.9111	.9240
3000			.615			.9120
4000			.962			.8927
			Sperm oil $\rho_{40}=0.8945$ g/cm³			
1	0	$\bar{1}.720$	$\bar{1}.256$	0.9894	1.0000	1.0227
100	0.079	.792	.374	.9835	.9934	
200	.150			.9781	.9876	1.0099
300	.220	.920		.9730	.9818	
400	.289	.981		.9685	.9768	
500		0.040	.531		.9722	.9925
750		.181	.649		.9618	.9794
1000		.318	.757		.9525	.9684
1500			.959		.9437	.9510
2000			0.149			.9368
2500			.327			.9241
3000			.481			.9127
4000			.792			.8926
			Pennsylvania oil $\rho_{40}=0.8524$ g/cm³			
1	0	$\bar{1}.660$	$\bar{1}.020$*	0.9901	1.0000	1.0178
100	0.119	.761		.9839	.9934	
250	.280	.904	.235*	.9752	.9841	1.0040
500	.536	0.131	.420*	.9632	.9711	.9908
750	.777	.346	.594*	.9529	.9599	.9786
1000	1.008	.551	.760*	.9440	.9504	.9672
1500		.955	0.070		.9340	.9485
2000		1.341	.369		.9196	.9330
2500			.661			.9196
3000			.953			.9082
4000			1.511			.8891

* Extrapolated.

[1] J. H. Hyde, Proc. Roy. Soc. **A97**, 240 (1920).
[2] M. D. Hersey and H. Shore, Mech. Eng. **50**, 221 (1928).
[3] R. V. Kleinschmidt, Trans. A.S.M.E. APM-50-4 (1928).
[4] P. W. Bridgman, Proc. Am. Acad. **61**, 57 (1926).
[5] R. B. Dow, Physics **6**, 71 (1935).
[6] R. B. Dow, J. Wash. Acad. Sci. **24**, 516 (1934).

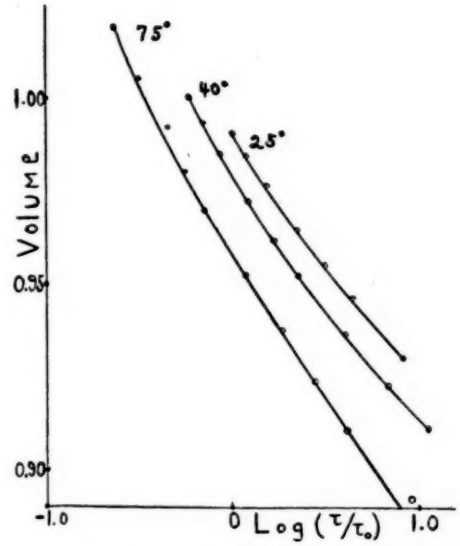

FIG. 1. Relative viscosity of lard oil as a function of volume.

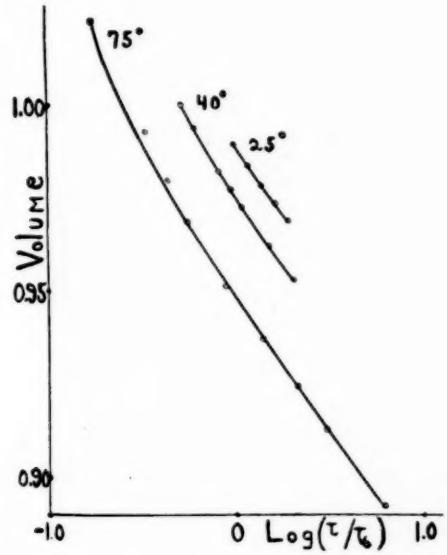

FIG. 2. Relative viscosity of sperm oil as a function of volume.

ture and t_0 the time of fall at atmospheric pressure at 25°. The reader is referred to the original papers for details of method and computation.

DISCUSSION

It is apparent at once on inspection of Figs. 1, 2, and 3, which are drawn from the data of Table I, that the relative viscosity increases greatly with comparatively small decrease of volume. Inasmuch as the figures are drawn from data of different observers, as mentioned previously, there is some doubt as to the experimental accuracy of the viscosity-volume curves. However, the writer's acquaintance with the method used by Kleinschmidt for the viscosity determinations leads him to estimate the inaccuracy of the curves to be not more than a few percent, which does not seriously limit their applicability. The lack of serious deviation of the points representing the experimental values from the smooth curves of the figures gives an indication of the probable degree of accuracy of the data.

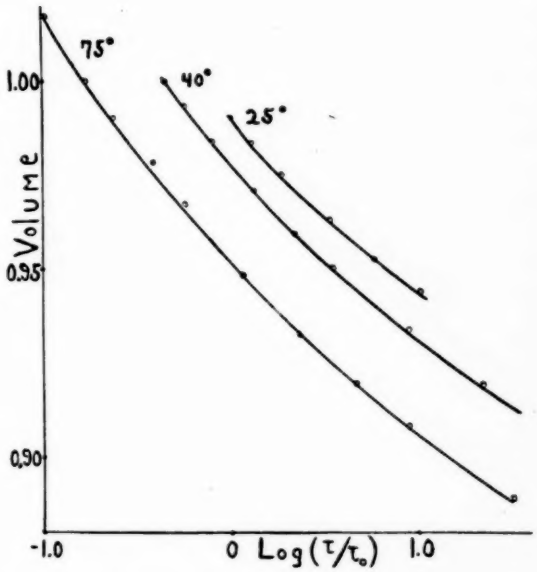

FIG. 3. Relative viscosity of Pennsylvania medium oil as a function of volume.

An interesting feature of the figures is the relative displacements of the viscosity-volume curves at 25°, 40° and 75°C. If viscosity were a function of volume only, the curves for each oil would coincide at all three temperatures. The figures show that this requirement is not satisfied in any case. The viscosity-volume curve for lard oil at 25° departs from the curve at 75° by an amount sufficient to change the viscosity by a factor of 2.3 at a volume of 0.99, and by a factor of 3.2 at a volume of 0.93. Similar curves for the Pennsylvania oil at 25° and 75° are even more relatively displaced; the discrepancy in viscosity varies from a factor of 3.8 at a volume of 0.99 to 7.6 at 0.94.

Of the theoretical relationships that have been proposed for viscosity as a function of volume, that of Batschinski[7] has been the most useful. His equation states that viscosity is related to the specific volume in the following way

$$\eta = c/v - \omega.$$

c and ω are characteristic constants of the liquid. Batschinski showed that if the change of fluidity of normal liquids, such as benzene and ethyl ether, was expressed with change of volume caused by change of either temperature or pressure, a linear relation resulted as demanded by his equation. But the data on viscosity and volume as functions of pressure were so limited in range of pressure available at that time, that both quantities could be fairly well expressed as linear functions of pressure. It is well known that such functions do not remain linear through the range of pressure now available.

Batschinski's equation has been used lately by Bingham and Brown,[8] Bingham and Coombs,[9] and Lederer[10] in deducing theories of viscosity. Although there is little experimental information concerning lubricants in this respect, R. N. J. Saal[11] in discussing the influence of pressure on the viscosity of a nonplastic, asphaltic bitumen, considered that his experimental data showed that the decrease of viscosity as the temperature rose was due to the effect of thermal expansion. Thus in addition to what has already been established without any assumption as to theory, namely, that viscosity is not a function of volume only, it is desirable to call attention to the failure of Batschinski' equation at high pressures, for this limitation does not seem to have been generaly established.

Bridgman[4, 12] has published viscosity-volume data for several normal liquids. His results gave curves similar to the figures of this paper. An examination of Batschinski's equation by substitution of Bridgman's data gives a general result that in no case is a linear relation obtained between fluidity and specific volume. Benzene, ethyl ether, pentane, etc., obey the Batschinski equation at atmospheric pressure, that is when the equation is applied for change of temperature, but at higher pressures the invalidity of the equation is beyond experimental error.

Consequently, on referring to Figs. 1, 2, and 3 again, it is not unexpected that the fluidity curves would not bear a linear relation to the volume, and the observed displacements of the curves show that the viscosity, or fluidity, is also a function of temperature. Accordingly, the constants c and ω of Batschinski's equation vary with pressure and temperature for these three oils. These data establish a point of much theoretical interest, namely that pressure and temperature changes affect viscosity differently.

Bridgman[13] in a recent paper on some of the theoretical aspects of high pressure phenomena has discussed the effects of temperature and pressure on the energy of solids, showing that in the case of NaCl the change of energy internal to the atom is nearly three times as great when a definite change of volume is brought about by a change of pressure as when brought about by a change of temperature. His explanation considers a compressible atom as demanded by a theorem of Schottky. It is likely that the fundamentals of the situation apply to liquids and give a possible explanation of the different effects of pressure and temperature on viscosity, although the problem remains to be treated quantitatively. The experimental evidence for the compressible atom is uncontrovertible to such an extent that Batschinski's conception of atomic volume constants cannot be valid over a wide experimental range. It is the desire of the author to call attention to these serious limitations of Batschinski's theory as demanded by the experimental data, rather than to question the usefulness of the relation at atmospheric pressure.

[7] A. Batschinski, Zeits. f. physik. Chemie **84**, 643 (1913).
[8] E. C. Bingham and D. F. Brown, J. Rheol. **3**, 95 (1932).
[9] E. C. Bingham and C. E. Coombs, Physics (New York Meeting).
[10] E. L. Lederer, Kolloid-Bei. **34–35**, 270 (1932).
[11] R. N. J. Saal, Proc. Wor. Pet. Congress, London, 521 (1934).
[12] P. W. Bridgman, Proc. Am. Acad. **66**, 185 (1931).
[13] P. W. Bridgman, Rev. Mod. Phys. **7**, 6 (1935).

Velocity-Gradient Methods in Rheology

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Since in a colloidal or quasi-plastic material, the viscosity is a function of the rate of shear, it seems best to determine the velocity-gradient across a section perpendicular to the direction of flow under shearing forces, and to determine the coefficient of viscosity under a given velocity gradient. An account is given of the experimental methods at present available for this purpose, and a method indicated by which the viscosity may be calculated from such measurements. The viscometers described comprise instruments based on the optical, electromagnetic, hot-wire and color-band principles, respectively.

THAT a colloid behaves abnormally under shearing stresses has been known since Bingham[1] first investigated the matter. As a consequence of this fact, any attempt to deduce a *coefficient of viscosity* for such a substance from measurements in either a capillary-flow or a concentric-cylinder apparatus will only produce qualitative results, for the viscosity is a function of the rate of shear, which will vary across a section of the flow. It was Hatschek[2] who suggested that if the velocity-gradient across a section of the fluid in motion could be measured, it would be possible to determine the coefficient of viscosity in terms of the velocity-gradient. In spite of ingenious attempts to assume some such function and to substitute it in the Poiseuille or Couette equations, as the case may be, and deduce the form of this function from the usual measurements of outflow or torque, respectively, it is not until one actually measures the velocity or its gradient from point to point across a section of the flow that one can calculate the viscosity as a function of the shear with certainty. The object of the present paper is to describe the methods at present available. They are all of quite recent origin. They may be grouped under four heads, *viz.*:

(1) *The photographic method.* Particles moving in the fluid reveal their relative velocity by the relative lengths of the streaks which their images make on a photographic plate during a certain exposure.

(2) *The electromagnetic method.* This depends on the induction produced by charged particles in the fluid moving in a magnetic field.

(3) *The hot-wire method.* The cooling of the wire is proportioned to the velocity at that point in the fluid.

(4) *The visual method.* By a color scheme imposed on the substance, it is made to exhibit the form into which an originally plane section is curved under shearing stress.

The photographic method was apparently first used by Porter and Nisi[3] in 1923 for studying the flow of air round obstacles on a small scale. They placed a ball bearing 3 mm (1/8″) diameter in a tube of square section at a point where a thin beam of light could be directed across the tube. To make the motion visible smoke was let into the tube at the level of this illuminated plane, and the camera directed in a direction perpendicular to it. When an exposure is made, the particles of smoke describe streaks on the photographic plate, whose lengths are proportional to their relative velocities. The method in some modification or other has been frequently employed in hydrodynamics since that time, though not often for the study of colloidal flow. In a sense, of course, the medium employed by Porter and his collaborators was colloidal, but the admixture of smoke was not at sufficiently high concentration to produce abnormal flow. The success of the method lies in the obtaining of the thin pencil of very brilliant light and in using the scattered light from the solid phase rather than the light directly transmitted through the tube. Pichot and Dupin[4] have used this method on a fluid partaking of both suspension and sol characteristics, consisting as it did of a 7 percent solution of gelatine in water with aluminum particles added to make visible the relative velocities of different parts of the fluid in a tube when an exposure was

[1] Bingham, *Fluidity and Plasticity* (1922), New York.
[2] Hatschek, *Viscosity of Liquids* (1928), London.
[3] Porter and Nisi, Phil. Mag. **46**, 754 (1923).
[4] Pichot and Dupin, Comptes rendus **192**, 1079 (1931).

made. From the only two photographs published by them (showing water and gelatine solution severally in the same tube) it is difficult to detect any considerable difference in the behavior of homogeneous and heterogeneous liquids.

By Faraday's laws of electromagnetic induction, when a conducting liquid is in motion in a magnetic field, an electromotive force is induced in it whose value is proportional to the product of the magnetic force and the velocity. Williams[5] attempted to measure the velocity-gradient across a tube in which an electrolyte was flowing by applying a magnetic field along a diameter and measuring the gradient of electromotive force along a perpendicular diameter on a sensitive galvanometer. Actually the instrument measures the voltage between two points and it is necessary to take one of these points on the interior surface of the tube, while the other is a probe, insulated save for the point, which is traversed along a diameter. The experimental tube was 1 cm diameter and the liquid, copper sulphate solution. A comparison is made of the theoretical voltage due to Poiseuille flow for a given distance of separation of the electrodes (expressed as a fraction of the diameter) and the observed voltage. It is not clear, however, how one could readily work back from a series of measured voltages to the unknown velocity distribution. With a string galvanometer, the method would serve for rapidly fluctuating velocities as in turbulent motion.

It is of interest to note that the method was used earlier on a large scale investigation of the tidal motion in the estuary of the River Dart (Devon).

We may conveniently include in this section the method of Alcock and Sadron,[6] since it is based on Maxwell's electromagnetic theory of light and was demonstrated by him in Canada balsam. A narrow beam of polarized light is doubly refracted by its passage through a gypsum plate. This refraction is modified by the subsequent transmission of the light through a stratum of the moving fluid, causing a shift of the interference bands arising from the double refraction to an extent proportional to the velocity of the stratum. As this method has been recently described in detail in this Journal, it is not proposed to repeat the description now.

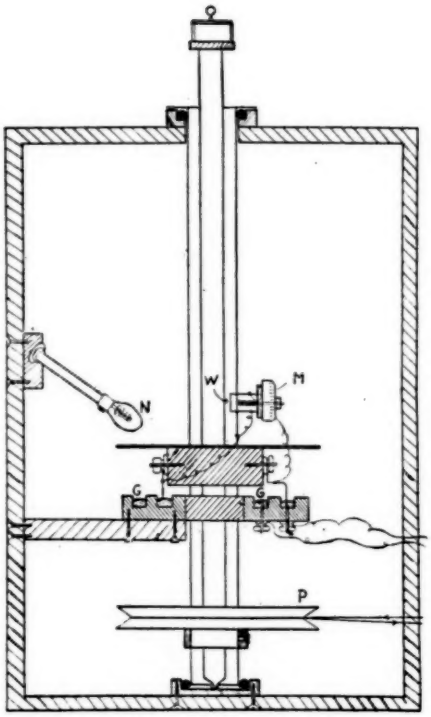

FIG. 1. Hot-wire anemometer.

An instrument which is still widely used in aerodynamics for measuring velocity is the Pitot tube. This consists essentially of a tube having a fine orifice facing upstream. The pressure difference between the air in this tube and in another shielded from the direct current (the static tube) is recorded on a sensitive manometer and is by Torricelli's law proportional to the square of the velocity. Kroepelin[7] has traversed such an anemometer across the end of a tube in which a gelatine solution was flowing at the place where it debouched upon the outflow reservoir and recorded small departures from the Poiseuille (parabolic) distribution.

A more sensitive anemometer for these purposes is that which depends upon the cooling suffered by a wire, electrically heated to about 25 degrees above the fluid temperature, when the fluid flows past it. The cooling is measured on a Wheatstone bridge in terms of the change of resistance experienced by the wire. Before use, the

[5] Williams, Proc. Phys. Soc. London **42**, 466 (1930).
[6] Alcock and Sadron, Physics **6**, 92 (1935).
[7] Kroepelin, Zeits. f. physik. Chemie **A149**, 291 (1930).

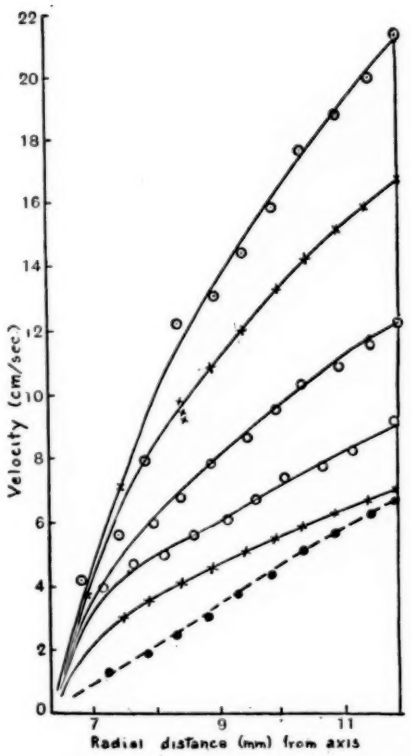

FIG. 2. Typical velocity-gradients in a suspension of starch in a solvent mixture of carbon tetrachloride and paraffin for four different rates of rotation of the outer cylinder of the hot-wire anemometer.

hot-wire anemometer must be calibrated by carrying it on a small *whirling arm* through the same *still* fluid contained in a tank. The calibration curve is obtained in the form of resistance as a function of the velocity. It is then ready to be applied to the measurement of velocity-gradients in the fluid in question. Instruments in which liquid flows through an oval tube, the wire being parallel to the flats of the oval section, or of the concentric cylinder type in which the wire is vertical and parallel to the axis of the cylinders, have been constructed by the writer, and one of the latter (Couette) type has been used by Dr. Tyler[8] and the writer[9] with some success for the study of velocity-gradients in suspensions.

The apparatus is shown in Fig. 1. The hot-wire W is of nickel 0.025 mm (0.001″) diameter and 1.5 cm (0.6″) long and is heated by a current of 0.3 amp. It is soldered to the ends of two fine needles inserted through ebonite sleeves in the outer cylinder which is rotated through the pulley P below. Electrical connection to the needles is assured by dippers working in the fixed annular rings of mercury GG mounted below the fork. The speed of this cylinder is observed by means of a Neon lamp N giving 50 flashes per sec. which illuminates the stroboscopic disk D. The hot-wire can be traversed across the annular space between the cylinders which are, respectively, 1.27 and 2.54 cm in diameter by means of the micrometer head M. The torque communicated to the inner cylinder may be taken up by a phosphor bronze suspension wire (not shown in the sketch) the twist on which was indicated by the usual mirror, lamp and scale. Fig. 2 shows typical velocity-gradients in a suspension of starch in a solvent mixture of carbon tetrachloride and paraffin (54.5 percent) which had the consistency of a paste (circles or crosses and continuous lines) for four different rates of rotation of the outer cylinder. On the same figure is shown one set (dots and broken line) for the solvent alone. Notice that although the latter, in accordance with theory, exhibits a nearly constant velocity-gradient through the annular space, the former shows a gradient growing steeper towards the inner cylinder, which is located on the left-hand ordinate of the figure. These curves are typical of the observations in starch suspensions as well as of clay pastes and gelatine solutions.

By using an Einthoven string galvanometer coupled through a transformer to the hot-wire circuit, it is possible to record the onset of turbulence in fluid flow at any point by noticing when the current through the wire begins to oscillate due to fluctuations in the heat losses from it engendered by turbulence.

Coming finally to the method by which the velocity-gradient is made visible by a dye, we find in a recent paper by Lawrence[10] application of this device to ammonium oleate solutions, known to show anomalous flow. By means of a special two-way cock, colored and uncolored fluid were alternately admitted to a tube. The dye used was the ammonium salt of Congo red. The head of the dye on entering the tube had a plane surface but after it had proceeded a little way into the flow tube it was distorted into a form which delineated the velocity-gradient. An exposure was

[8] Richardson and Tyler, Proc. Phys. Soc. London **44**, 142 (1933).

[9] Richardson, *Les Appareils à Fil Chaud* (1934), Paris.

[10] Lawrence, Proc. Roy. Soc. **A148**, 59 (1935).

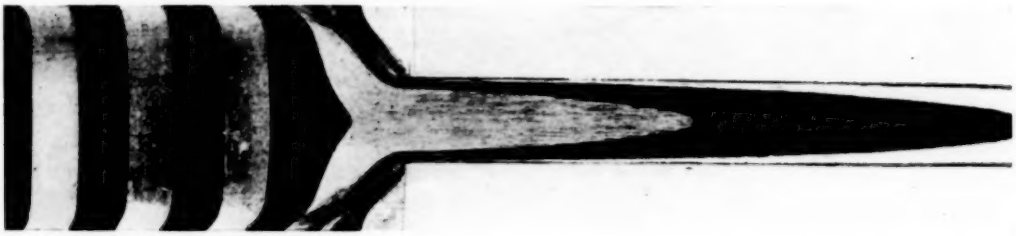

FIG. 3. Photograph of one of Pearson's metal billets extruded through a die.

then made and the resulting photograph, when enlarged, enabled the required velocity-gradient to be measured up. In a homogeneous fluid the heads of the colored sections would, of course, have been parabolas, but in the colloids deviations from these curves were obtained.

As another instance of the application of the visual method may be cited the use of a painted or etched pattern in the study of the extrusion of ceramic materials or metals through dies. This method seems to have been first applied by Tritton[11] to plasticine, alternate layers of two colors of which were put in a press and forced out through a hole. Mr. Pearson of the Metallurgical Department of this University has studied the extrusion of alloys by such a method, although being solid much greater pressures are required than with any of the other media we have mentioned. Pearson took a "billet" of the metal, cut it down the axis, painted the exposed plane surface of one of the half cylinders thus formed with ink in transverse stripes and put the two halves together again. The reunited billet was then placed in the barrel of a press which it just fitted, and the metal extruded through a die of aperture 1 cm diameter at the bottom of the press. As the alloy "flowed out," the stripes were distorted into shapes which represented the velocity-gradients under the given "head" of pressure. The pattern was exposed by separating again the two halves of the billet. A photograph of one of Pearson's extruded billets is shown (on its side) in Fig. 3.

In attempting a critique of the various methods that he has described above, the author is faced with the difficulty that with only two methods—and one of them his own—is a systematic measurement of a series of gradients available. The remaining workers have been content to show isolated specimens of the capabilities of their devices. There are, however, certain directions in which comparisons may be useful. One question which the colloid physicist will be sure to ask is as to the extent with which the measuring devices will interfere with the flow to be observed. Thus, in applying the photographic method one may have to introduce strongly light-scattering particles into the medium, which may change its properties. On the other hand this same method is well adapted to the study of systems which by their very nature contain solid particles, such as paints. In the electrical and hot-wire methods the electrodes may cause some interference, but since they may be formed of quite fine wires this source of trouble is not prohibitive. To the extent that the hot-wire is above the temperature of the surrounding fluid it may cause local heating and convection currents, but the excess of temperature is not more than 25 degrees and need not exceed 10 degrees. The chief difficulty in the color method appears to lie in the discontinuity in the flow at the change-over from one supply to the other, although this can be obviated by a well-designed two-way cock. The method of Lawrence requires the original colloid to be transparent, as does also that of Alcock and Sadron, while the method of Williams is restricted to electrolytes. Many of the authors have tested their respective instruments on an homogeneous fluid in streamline flow, and this is certainly a good test of the freedom of the apparatus from interference to the flow, which would at once be apparent as a deviation from parabolic distribution.

As typical of the types of flow recorded in tubes below the critical velocity we have grouped three curves on Fig. 4: (*A*) Parabolic distribution in paraffin, recorded by hot-wire, (*B*) a somewhat flattened curve in ammonium oleate, recorded by

[11] Tritton, J. Inst. Met. **26**, 250 (1921).

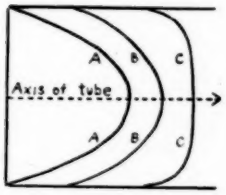

FIG. 4. Velocity distributions in tube flow. *A*, parabolic distribution in paraffin; *B*, a somewhat flattened curve in ammonium oleate; *C*, "plug flow" in extruded plasticine.

Lawrence's dye method, (*C*) "plug flow" in extruded plasticine, shown by the shape of the head of the emergent stem.

It will probably be asked how these data may be used to measure the viscosity of the substance. To do this it is necessary to obtain a formula for the velocity-gradient and exhibit how the viscosity varies with this by means of a graph. Thus if the apparatus is of the flow-tube type, the forces in equilibrium on a cylinder of radius r and of unit length are

$$\pi r^2 p = 2\pi r\eta \cdot dv/dr,$$

where p is the pressure inducing flow and dv/dr is the velocity gradient and η the coefficient of viscosity. Therefore η is proportional to $pr/dv/dr$ and we only need to plot this latter quantity against dv/dr to exhibit the way in which the viscosity varies with gradient.

In the case of the concentric cylinders, the velocity gradient at any radial distance being $rd\omega/dr$, where ω is the angular velocity of the outer cylinder, the moment of the annulus about the axis is $2\pi r^3\eta d\omega/dr$ per unit length, and this moment is constant for all annuli, so that the torque τ is proportional to $r^3\eta d\omega/dr$. Thus $\tau/(r^3 d\omega/dr)$ should be a measure of the relative viscosity. Thus from Fig. 2, the slope of the *angular velocity* curves may be plotted against r,

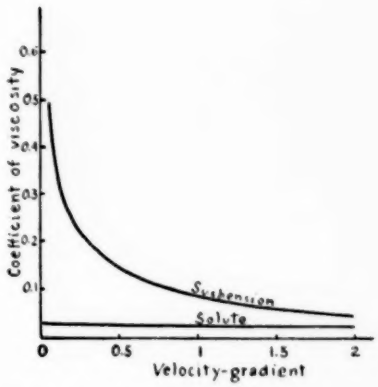

FIG. 5. Variation of viscosity with velocity-gradient.

and from this another curve of $\tau/(r^3 d\omega/dr)$ could be plotted against $rd\omega/dr$, τ being known from the twist on the inner cylinder. This curve is shown on Fig. 5 and accordingly shows us how the viscosity varies with velocity-gradient. The horizontal line shows the viscosity of the solvent.

Such methods as described in this paper may become more common in rheology in the near future, and may lead to the coefficient of viscosity for colloidal substances being defined at a standard velocity-gradient, for example 1 cm/sec. per cm. This is certainly preferable to the methods by which substances are put successively into a viscometer without any attempt to see that they are tested at comparable velocity-gradients, so that the two substances are being compared at varying and quite unknown rates of shear. Although technical viscometers are favored by industrial chemists on account of their simplicity and rapidity of working, it is to be feared that any results they may obtain with a substance whose viscosity varies in a fashion similar to that shown in Fig. 5—and this class includes a great many industrial products—must be quite valueless.